



ELECTRON TRANSFER REACTIONS WITHIN ZEOLITES: PHOTOOXIDATION OF STILBENES

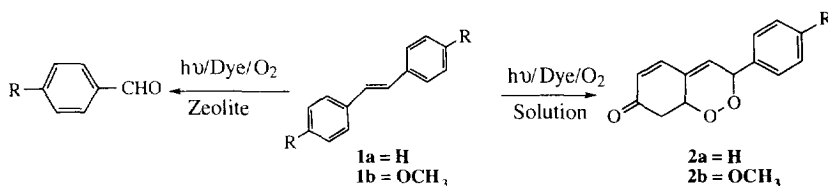
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Oxidation of stilbenes included in zeolites is much more efficient than in isotropic organic solvent. Oxidation efficiency depends on the cation and the presence of intra-zeolite water. Electron transfer from the oxidant stilbene to the excited dye molecule is suggested to initiate a non chain oxidation process. Copyright © 1996 Elsevier Science Ltd

Unique alterations of photochemical and photophysical processes of zeolite included organic guest molecules have been achieved by judicious use of inorganic cations present within the supercages of X and Y zeolites.¹ In this Letter, we show that it is possible to situate two dissimilar organic molecules near one another within zeolites in such a way that an interaction between the two may develop upon photoexcitation. We had established earlier that organic cations such as oxazine (Nile blue A, oxazine 170 and oxazine 1) and thiazine (methylene blue, thionin and methylene green) dyes can be exchanged within X, Y and L zeolites.^{2,3} Ability to cation exchange dye molecules within zeolites provided us an opportunity to investigate the oxidation of a variety of olefins adsorbed within zeolites.⁴ This study was also prompted by recent reports by Frei and co-workers on the oxidation of hydrocarbons within zeolites by visible light.⁵ Generality of this elegant process is yet to be established.

In this study, we have used thionin, methylene blue, methylene green, Nile blue A, oxazine-170, oxazine-1, pyronin Y, acridine orange, crystal violet, rhodamine-6G and safranin-O as dyes and *trans*-stilbene (**1a**) and *trans* 4,4'-dimethoxystilbene (**1b**) included within X and Y zeolites as oxidants (Scheme 1). Of these, only thionin, methylene blue and methylene green were effective as sensitizers for the oxidation of **1**. A general procedure was adopted for the exchange of inorganic cations of the zeolite with the cationic thiazine and oxazine dyes: About 250 mg of unactivated cation exchanged X or Y zeolite was dropped into an aqueous solution containing 1.25 mg of the dye. The colored aqueous solution became transparent when the solution was stirred with zeolite for about 3h. The above solution was centrifuged and the transparent aqueous solution was decanted. The colored residue was washed a number of times (5 x 20 ml) with water till no dye was extracted from the zeolite into aqueous layer. The dye-zeolite complex (250 mg) prepared as above (and characterized by diffuse reflectance spectra) was dried on a vacuum line with mild heating (<90°C) and taken in hexane (20 ml) with the olefin (5 mg) and stirred overnight. The colored zeolite adsorbed with olefin was filtered, washed with excess hexane (100 ml) and dried. The complex thus prepared containing both the dye (< one dye molecule per ~25 supercages)⁶ and the olefin (one molecules per ~5 cages) was photolyzed as a hexane slurry under oxygen atmosphere with a 450 W mercury lamp through a Corning Glass filter (#3-72, > 420 nm). Products were extracted with ether (20 ml) and analyzed by GC.



Scheme 1

Consistent with previous reports,^{7,8} oxidation of either *trans* stilbene or *trans* 4,4'-dimethoxystilbene (1 mg), sensitized by methylene blue or thionin (2x10⁻³ M) in methylene chloride/methanol solution (2 ml) was inefficient—about 50% conversion was achieved in about 6 h of irradiation (> 420 nm). To our surprise, when the oxidation

was conducted within alkali cation exchanged X or Y zeolites (1mg of olefin and <0.1 mg of dye in 50 mg of zeolite suspended in 2 ml of hexane), the oxidation was very efficient (Figure 1). For example, quantitative conversion to the corresponding aldehyde was achieved within 30 mts of irradiation in Li Y. We recognize that owing to absorption differences between homogeneous and heterogeneous media, direct comparison of the efficiencies of oxidation between solution and zeolite media is not completely meaningful. However, the large difference in efficiency of oxidation between the two media observed in this study is beyond experimental artifacts. Another, unexpected observation relates to the role of the cation. As seen in Figure 1, the efficiency of oxidation dependent on the cation used. While the oxidation is efficient in Li^+ and Na^+ exchanged X and Y zeolites, it was very inefficient in Rb^+ and Cs^+ exchanged zeolites. Most importantly, presence of water within zeolite cavities completely prevented the oxidation.

It is important to note that no oxidation occurred within dye exchanged zeolites in the absence of light. Further, exposure (as hexane slurry) of stilbenes trapped within zeolites to visible light did no result in any reaction. It is quite likely that when the zeolite supercage is filled with hexane no charge stabilization of oxygen-olefin complex occurs. In any case, control experiments have clearly indicated that in order for efficient oxidation to occur it is important to have both the dye and the zeolite.

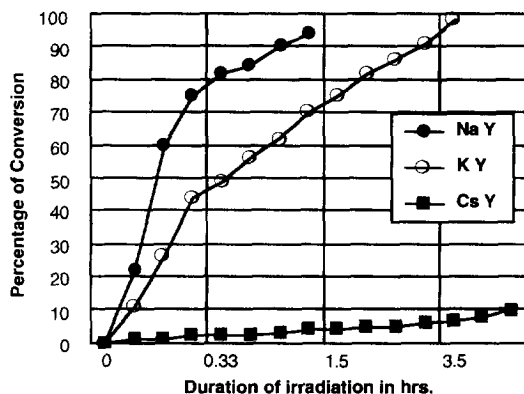
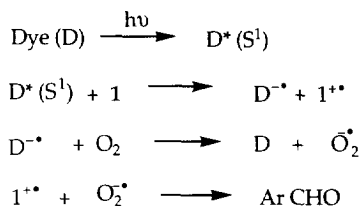


Figure 1: Dependence of conversion on the cation during irradiation of **1b** and thionin included in Y zeolites.

The oxidation, we believe, is initiated by an electron transfer from either **1a** or **1b** to the singlet excited dye. This is consistent with the results reported in homogeneous media. In homogeneous solution, *trans* stilbene and *trans* 4,4'-dimethoxystilbene are oxidized to the corresponding endoperoxide (**2**) by singlet oxygen (energy transfer pathway) and to the corresponding aldehyde via superoxide anion (electron transfer pathway) (Scheme 1).⁹⁻¹¹ Specifically with respect to stilbenes, methylene blue, has been suggested to act as an electron transfer sensitizer in solution.⁷ The observation that the oxidation within zeolites is quenched by DABCO and N,N-dimethyl aniline but not by either 2,3-dimethyl but-2-ene or β -carotene supports the conclusion that the oxidizing species within zeolite is not singlet oxygen. We believe that DABCO and N,N-dimethylaniline quench the reaction by competing with **1** at the primary electron transfer step. Consistent with the above suggestion, oxidation of zeolite included **1a** and **1b** to the aldehyde can be effected by the classical electron transfer sensitizer, 9,10-dicyanoanthracene (DCA). However, in homogeneous media, DCA has been shown to act also as a singlet oxygen sensitizer^{10b} To distinguish between the two possibilities—energy transfer and electron transfer—we carried out the following experiments. We reasoned that the quencher under these two conditions are different—in one case it is oxygen and in the other it is **1**. If the primary step is electron transfer, the efficiency of oxidation must be dependent on the occupancy number of DCA; higher occupancy level will bring DCA* closer to the quencher **1**. On the other hand, if energy transfer to oxygen is important, occupancy level may not be directly related to the efficiency of oxidation. Experiments carried out with various loading levels (<S> varied between one molecule per 32 cages to one molecule per 4 cages) of DCA allowed us to conclude that the oxidation within zeolites involve electron transfer pathway.



Scheme 2

As would be expected for an electron transfer pathway, oxidation efficiency in the case of **1b** increased with the increased loading level of the sensitizer (Figure 2). Also, when irradiation of a hexane slurry containing dye and **1b** localized in different Na Y particles was conducted no oxidation occurred. Suggested sequence of processes involved in the conversion of **1** to the corresponding aldehydes are listed in Scheme 2. This is identical to the one proposed by Foote for electron transfer mediated oxidation in solution.¹⁰

As illustrated in Figure 1, larger (heavier) cations have a pronounced effect on the oxidation efficiency.

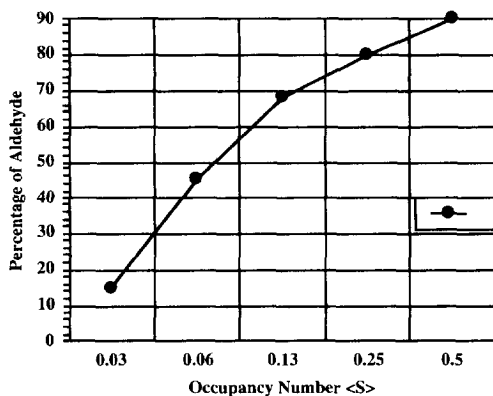


Figure 2: Dependence of oxidation efficiency of **1b** included within Na Y on the occupancy number (<S>) of 9,10-dicyanoanthracene.

Oxidation is very slow within Cs Y and Cs X. Influence of cations on photochemical reactivity of included guest molecules is known.¹ Cations have been speculated to influence the chemical behavior of guest molecules through 'light atom' effect, 'heavy atom' effect or through 'size/space' effect.^{1c} Enhanced reactivity within Li⁺ and Na⁺ exchanged zeolites can not be attributed to the light atom effect, *i.e.*, to the binding of the cation to the π -cloud; this would be expected to decrease rather than increase the reactivity. Decrease in reactivity within Cs Y and Cs X can be due to shorter lifetime of excited singlet state of thionin brought forth by heavy cations such as Cs⁺ (by enhancing the intersystem crossing from S₁ to T₁). However, the fluorescence and the excited singlet lifetime (~2.4 ns) of thionin was independent of the cation.¹² By elimination of the above two possibilities, we are led to suggest that it is the size of the cations that precludes close contact between the dye and **1** that is needed for efficient electron transfer.¹³

Oxidation of **1** within Na Y and Na X is extremely sensitive to the presence of water within the zeolite. Unless the zeolite is very dry no oxidation occurred. We suggest that water controls the oxidation by controlling the status and location of dye molecules within zeolite.¹⁴ We have shown earlier that the presence of water favors aggregation of dyes within zeolite cavities³ Aggregated dyes are known to be poor sensitizers since they undergo efficient self-quenching in the excited singlet state.¹⁵ Further, presence of water molecules might displace **1** to the surface thus preventing close interaction between the excited dye molecule and the quencher.¹⁴ It is also likely that intra-cavity water quenches the singlet oxygen leading to inefficient oxidation of stilbenes. Experiments are underway to understand these features.

We speculated that the efficient oxidation obtained within Li⁺ and Na⁺ exchanged zeolites might be due to a chain process. Oxidation via a chain mechanism is known¹⁶ To test this hypothesis, we carried out oxidation at different loading levels of **1b**. Thionin was maintained at a level of 1 molecule per ~20 cages and **1b** was varied

between 1 molecule per 6 supercages to 1 per 1 supercage. Irradiation of these samples under identical conditions gave nearly ($\pm 5\%$) the same amount of aldehyde. This rules out a chain process under our conditions.

What are the advantages of using zeolite as the medium as opposed to organic solvents? Results presented in this Letter provide a new approach towards enhancing the efficiency of oxidation of olefins. Enhanced efficiency is the result of 'localizing/confining' the sensitizer and the oxidant within the restricted space of a zeolite. This technique provides an effective high 'local concentration' which is difficult to achieve in homogeneous media. To our knowledge, this is the first example in which a chemical transformation has been achieved by assembling three species (dye, olefin and oxygen) within the internal structure of a zeolite.¹⁷ We are extending our studies to other systems with the aim of obtaining regio, diastereo and enantioselective products during oxidation within zeolites.

References

- For a few selected reviews see: (a) Turro, N. J. *Pure & Appl. Chem.* **1986**, *58*, 1219. (b) Ramamurthy, V.; Eaton, D. F.; Caspar, J. V. *Acc. Chem. Res.* **1992**, *25*, 299. (c) Ramamurthy, V. in *Photochemistry in Organized and Constrained Media*, Ramamurthy, V. Ed., VCH, New York, 1991, pp. 429-493.
- Ramamurthy, V.; Eaton, D. F.; Sanderson, D. R. *J. Am. Chem. Soc.* **1993**, *115*, 10438. 23.
- (a) Calzaferri, L. G.; Gfeller, N. *J. Phys. Chem.* **1992**, *96*, 3428. (b) Wohrle, D.; Schulz-Ekloff, G. *Adv. Mater.* **1994**, *6*, 875.
- Results on the oxidation of acyclic and cyclic alkenes will be presented elsewhere: Li, X.; Ramamurthy, V. unpublished results.
- (a) Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1993**, *115*, 7501. (b) Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1994**, *116*, 1812. (c) Sun, H.; Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1994**, *116*, 7951. (d) Blatter, F.; Moreau, F.; Frei, H. *J. Phys. Chem.* **1994**, *98*, 13403. (e) Blatter, F.; Sun, H.; Frei, H. *Cat. Lett.* **1995**, *35*, 1. (f) Blatter, F.; Sun, H.; Frei, H. *Chem. Eur. J.* **1996**, *2*, 113.
- The exact amount of the dye present within zeolite is unknown since considerable amount of dye was washed from zeolite with water. The loading level given is the maximum that is possible with the amount of dye that is taken.
- Manring, L. E.; Erikson, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 4275.
- (a) Rio, G.; Berthelot, J. *Bull. Chim. Soc. Fr.* **1969**, 3609. (b) Schultz, A. G.; Schlessinger, R. H. *Tetrahedron Letters* **1970**, 2731. (c) Politzer, I. R.; Griffin, G. W. *Tetrahedron Letters*, **1973**, 4775. (d) Matsumoto, M.; Dobashi, S.; Kondo, K. *Tetrahedron Letters* **1977**, 2329.
- (a) Erikson, J.; Foote, C. S.; Parker, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6455. (b) Boyd, J. D.; Foote, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 6758.
- (a) Foote, C. S. *Tetrahedron* **1985**, *41*, 2221. (b) Kanner, R. C.; Foote, C. S. *J. Am. Chem. Soc.* **1992**, *114*, 678 and 682. (c) Erikson, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083.
- Kwon, B. M.; Foote, C. S.; Khan, S. I. *J. Org. Chem.* **1989**, *54*, 3378.
- Ramamurthy, V.; Caspar, J. V.; Eaton, D. F.; Kuo, E. W.; Corbin, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 3882.
- Turro, N. J.; Zhang, Z. *Tetrahedron Letters* **1987**, *28*, 5637.
- Zhang, Z.; Turro, N. J.; Johnston, L. J.; Ramamurthy, V. *Tetrahedron Letters* In press.
- (a) Lewis, G. N.; Goldschmid, O.; Magel, T. T.; Bigeleisen, J. *J. Am. Chem. Soc.* **1943**, *65*, 150. (b) Rabinowitch, E.; Epstein, L. F. *J. Am. Chem. Soc.* **1941**, *63*, 69. (c) Herkstroeter, W. G.; Martic, P. A.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 3583. (d) Sens, R.; Drexhage, K. H. *J. Luminiscence* **1981**, *24*, 709. (e) Isak, S. J.; Eyring, E. M. *J. Phys. Chem.* **1992**, *96*, 1738.
- (a) Barton, D. H. R.; Leclerc, G.; Magnus, P. D.; Menzies, I. D. *J. Chem. Soc., Chem. Comm.* **1972**, 447. (b) Tang, R.; Yue, H. J.; Wolf, J. F.; Mares, H. *J. Am. Chem. Soc.* **1978**, *100*, 5248. (c) Kabe, Y.; Takata, T.; Ueno, K.; Ando, W. *J. Am. Chem. Soc.* **1984**, *106*, 8174. (d) Nelson, S. F. *Acc. Chem. Res.* **1987**, *20*, 269. (d) Lopez, L.; Troisi, L.; Rashid, S. M. K.; Schapp, A. P. *Tetrahedron Letters* **1989**, *30*, 485.
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